SATURATED HYDROCARBON POLYMERIC BINDER FOR

ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN

QUARTERLY REPORT NO. 4

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I. OBJECTIVE

Union Carbide Corporation, Plastics Division has agreed to provide, on a level of effort basis, between 100.8 and 106.8 direct man months of effort to assist the Jet Propulsion Laboratory in the development of a new or improved polymeric binder for advanced solid propellant and hybrid solid grains. The detailed objectives are described in Quarterly Report No. 1.

II. SUMMARY

During the past quarter various factors which might adversely influence the attainment of satisfactory levels of carboxyl content in the prepolymer have been examined critically. The choice of solvent in the molecular weight determination had previously been found to be very critical. The titrimetric procedure for determining neutralization equivalent was found to be somewhat lacking in precision and accuracy and was altered. This had only a small effect on the measured value of N. E.

The possibility that polymeric anhydrides were being formed during sample work-up was tested using an available analytical determination for anhydrides. No evidence for the presence of anhydrides was found.

The monomer, neohexene, was analyzed thoroughly for the presence of chain transfer impurities--none were found.

The oxygen functionality of the prepolymer made with DMAB initiator was found to decrease with increasing batch reaction time, indicating a changing reaction environment. Further examination of these products demonstrated the presence of small amounts of polymer containing a high concentration of carboxyl groups, which was not compatible with the copolymer. It is suspected that this incompatible polymer contains methacrylic acid, derived from methyl methacrylate which can arise from the disproportionation of two initiator radicals. The other disproportionation product from DMAB radicals is methyl isobutyrate, which is a chain transfer agent. If correct, this suggests as a possible solution that we rely on symmetrical chain transfer agents such as dithiodibutyric acid as a major source of functionality and keep initiator concentration minimized. The implications of this discovery are being vigorously prosecuted.

III. SCOPE OF PROJECT

The scope of this work has not changed from the program outlined in the work statement. The major emphasis has been placed on obtaining an adequate understanding of the reaction requirements for making a copolymer having the required level of functionality. A small, continuous reactor is being placed in service to better define these reaction variables under steady state conditions.

IV. INTRODUCTION

In our third quarterly report the molecular weight distributions of a variety of ethylene-neohexene copolymers, determined by the new technique of gel permeation chromatography, were presented. The ratio of weight average molecular weight to number average molecular weight, $\bar{M}_w/\bar{M}_n$, was found to be between 1.2 and 1.5 for the samples studied. These products are very narrow in molecular weight distribution.

Molecular distillation was used to fractionate ethylene-neohexene copolymers in the molecular weight range 200-800. The fractions obtained were narrow in molecular weight distribution.

Data were generated which provide strong reason for preferring to run molecular weights of carboxylic acid containing prepolymers in polar solvents such as tetrahydrofuran.

DEAB, diethyl, α, α' - azobisisobutyrate was used as an initiator for ethylene neohexene copolymerization. Carboxylic acid functionalities, based on molecular weights measured in tetrahydrofuran, were near unity, suggesting that this initiator is a chain transfer agent.

In order to decrease the likelihood of chain transfer at the alkoxy group in DEAB, it was decided to synthesize the dimethyl ester of azobis isobutyric acid, DMAB. This synthesis proved to be quite facile and the substance was prepared in several hundred gram quantity for use in copolymerization studies.

The following sections describe various experiments which have been performed during this quarter to further define the factors which control copolymer functionality.

V. TECHNICAL DISCUSSION

A. Factors Influencing Functionality of Ethylene-Neohexene Binder

Although choice of initiator is a basic factor in determining the carboxyl functionality of these prepolymers, other factors are also critical, such as purity of reactants and solvents and reliability of analytical data. In previous reports we have described the large effect on measured functionality of the type of solvent used in determining the number average molecular weight of the prepolymer. In general, molecular weights determined in benzene are almost twice as high as those determined in a polar solvent such as tetrahydrofuran. This is due to the marked tendency of the carboxyl groups in these polymers to form hydrogen bound aggregates in non-polar solvents. The use of "benzene" molecular weight data was shown to result in erroneously "high" carboxyl functionalities.

1. Examination of Method of Determining N. E.

If we recall that functionality (F) is defined as:

$$\text{Functionality (F)} = \frac{\text{No. Avg. Mol. Wt. } (\bar{M}_n)}{\text{Neutralization Equivalent (N.E.)}}$$

it is apparent that a low functionality will be observed if $\bar{M}_n$ is erroneously low or N. E. is erroneously high. The drastic effect of using a non-polar solvent in the determination of $\bar{M}_n$ has already been discussed. In this report we will describe experiments which have been carried out in order to reappraise our carboxyl terminated ethylene-neohexene copolymers.

Our standard procedure was to titrate a xylene solution of the prepolymer with a solution of KOH in ethanol to the phenolphthalein end point. This method was found to have several deficiencies:

1. Ethanolic KOH titrant is not stable, discolors on standing and must be frequently restandardized.

2. The color change of phenolphthalein does not occur exactly at the time equivalence point.

3. The potentiometric end point is not sharp.

4. KOH is not basic enough to quantitatively titrate all of the acidic groups present.

Fortunately, deficiencies (1) and (2) tend to cancel one another.

After considerable investigation we have adopted a new procedure in which the polymer is dissolved in methyl ethyl ketone and titrated with 0.1 normal tetrabutyl ammonium hydroxide in isopropanol. The end point can be determined either potentiometrically or visually. Using glass versus standard calomel electrodes a very sharp end point is observed at -550 millivolts. Thymol blue undergoes its color change exactly on the vertical portion of the potentiometric titration curve and can be used successfully except when the polymer solution is highly colored.

Using this revised procedure it has been found that neutralization equivalents are somewhat lower than the results from the older method, which, in effect, increases the concentration of COOH present. An example of how this affects N. E. and functionality is given below:

	Neutralization Equivalent			Functionality	
Sample No.	Old Method	New Method	$\bar{M}_n$	Old	New
23-EMS-4	789	779	779	0.99	1.00

It is seen that the error in the old data was small, at least in this instance. Because of the ease of obtaining reproducible results with the new procedure, it will be used as the standard method in this and subsequent reports.

2. Polymeric Anhydride Formation

Another possible cause of low functionality in these copolymers is the formation of intermolecular anhydride groups during work-up procedures. Our suspicions were aroused by unexplainable increases in viscosity of certain samples of prepolymer during work-up and the occurence of infra-red absorptions similar to the anhydride doublets in the 5 micron region. Obviously anhydrides which might not hydrolyze rapidly during N. E. determination would raise the N. E. of the sample and also raise the observed molecular weight.

Anhydrides are known to react quantitatively and rapidly with morpholine to give morpholides and the corresponding carboxylic acid. Morpholine may be titrated with strong acid in the presence of carboxylic acids. Johnson and

Funk [Anal. Chem., 27, 1464 (1955)] have published a method
for the analysis of anhydrides in the presence of the corre-
sponding acids based on these facts. Using this procedure
we found no measurable amount of anhydride in a copolymer
sample (hydrolyzed 23 EMS-11) which exhibited the infra-red
absorptions "characteristic" of anhydrides.

To further strengthen the evidence that anhydrides
are not a problem, we subjected a sample of a known difunctional
polymer (EMPOL-1010 dimer acid) to a more severe thermal cycle
than ever used in work-up of our samples: 6 hours at 150°C
under vacuum in a rotary evaporator. There was no change in
neutralization equivalent as a result of this treatment. If
anhydrides formed they were completely hydrolyzed during the
titration procedure.

3. Gas Chromatographic Analysis of Neohexene Monomer

Although we were given positive assurance by the
vendor that the polymerization grade neohexene we have been
using is very pure, it seemed prudent to verify this fact
ourselves. The presence of certain impurities could result
in chain transfer and lead to low carboxyl functionality in
the prepolymer. Neohexene is one of 13 isomers of hexene,
(not counting cis-trans isomers) and is the only one which
does not have allylic hydrogen atoms. The presence of any
of these isomers would lead to chain transfer reactions which
would have an adverse affect on functionality. Because of
the possibility that one or more of these isomers might
be formed from neohexene by isomerization during its manufac-
ture, it was decided to examine neohexene using a high
resolution gas chromatograph.

The 13 isomers of hexene are listed in Table I A,
(Appendix) with their boiling points and their structural
formulas. Neohexene is much lower in boiling point than the
other isomers. Samples of five of these isomers were pur-
chased covering the whole range of boiling points.

A Perkin-Elmer Model 226 gas chromatograph was used
to analyze our neohexene as well as each of the 5 isomeric
hexenes. Then a synthetic mixture of neohexene and the other
5 isomers was prepared and analyzed under the same conditions.
The gas chromatograph was equipped with a 300 ft. long column
of 0.01 inch I. D. stainless steel capillary tubing internally
coated with Dow-Corning 550 silicone grease. The column was
operated at 40°C under an inlet pressure of 15 psi of carrier
gas. The column achieves a separation efficiency of 300,000
theoretical plates.

A chromatogram showing the purity of our poly-
merization grade neohexene is shown in top graph of Figure 1.
(Appendix). The lower chromatogram is the result obtained
when the synthetic mixture of 6 isomers was analyzed. Note
the excellent resolution of the different isomers which are
eluted from the column in order of their respective boiling
points, neohexene first and 2,3 dimethyl butene-2 last.

Immediately following the elution of the neohexene
peak in the upper chromatogram, the sensitivity of the detection
system was increased by a factor of 500. Even at this great
sensitivity, no other components other than neohexene were
detectable. A peak of the order of two times the size of the
random noise in the signal from the detector would represent
only 70 parts per million of the injected sample.

From these studies we have concluded that the
neohexene we are using is not contributing any impurities
of any consequence to the polymerization system.

B. Preparation of Ethylene-Neohexene Copolymers With
DMAB Initiatior.

The synthesis of the azo initiator DMAB was described
in our previous quarterly report. In order to become familiar
with the behavior of DMAB in polymerization, three preliminary
runs were made at 80°C at three different pressures. The
essential data are tabulated in Table I. The low pressure
runs produced prepolymer in the molecular weight range of
interest, while the 20,000 psi run gave a polymer of very high
viscosity. The oxygen functionality of these products was
low as was the carboxyl functionality after hydrolysis of the
terminal esters.

These preliminary results, along with earlier results
with DEAB initiated products, led us to suspect that changes
in the reaction environment during these batch runs might be
responsible for the observed functionalities. In order to
check this possibility we carried out a series of polymeri-
zation runs at 80°C and at 90°C, in which the reaction time
was varied from 15 minutes to several hours. This procedure
was in lieu of removing samples periodically from one long run,
which is impractical due to the pressure involved.

The results of these runs are summarized in Table II.
At both temperatures the oxygen functionality was a function
of reaction time, from which it was surmised that changes in

TABLE I
PRELIMINARY RUNS WITH DMAB

Run No. 23 EMS- Initial Charge	20	21	22
Solvent	Benzene	Benzene/TBuOH	Benzene
Solvent, wt., gms.	29.6	0.00	11.1
Neohexene, gms.	510	665	605
Initiator, gms.	1.6	2.7	3.7
Ethylene, gms.	192	279	229
Fed During Run			
Solvent, gms.	267	293	99.6
Initiator, gms.	14	–	33.2
Reaction Conditions			
Temperature °C	80	80	80
Pressure	2650	20,000	4375
Reaction Time, hrs.	23	5.6	23
Productivity			
Yield, gms.	112	71	221
% Conversion	22	7.5	26.5
Rate, %/hr.	5	1.3	1.2
Properties Before Hydrolysis			
Molecular wt.	1107	3462	–
Brookfield Visc.			
Centipoise	15,100	$>$400,000	13,200
Wt. % Oxygen	3.32	0.93	–
O_2 Functionality	1.15	1.01	–
Properties After Hydrolysis			
Molecular Weight	1127	–	1099
Neutralization Equiv.	1199	–	1131
COOH Functionality	0.94	–	0.97

TABLE II

EFFECT OF REACTION TIME ON OXYGEN FUNCTIONALITY OF PREPOLYMER

RUN #23 EMS	33	34	31	32	44	41	42	37
INITIAL CHARGE								
Benzene, Gms	30 ⟶			⟶	33 ⟶			⟶
Neohexene, Gms	510 ⟶			⟶	501 ⟶			⟶
DMAB, Gms	1.6 ⟶			⟶	1.7 ⟶			⟶
Ethylene, Gms	188 ⟶			⟶	189 ⟶			⟶
FED DURING REACTION								
Benzene, Gms	25.8	77.3	136.7	218.5	48.5	87.3	87.4	294
DMAB, Gms	1.4	4.1	7.2	11.5	2.55	4.56	6.26	15.6
REACTION CONDITIONS								
Temperature, °C	80 ⟶			⟶	90 ⟶			⟶
Initial Pressure	1000 psi ⟶			⟶	1050 psi ⟶			1000 psi
Final Pressure	1000	1150	1000	2000	1050	1050	1225	3350 psi
Time, Hrs.	0.5	1.5	4.0	6.0	.25	.50	1.0	4.5
PRODUCTIVITY								
Yield, Gms.	4	12	25	53	5	9	22	87
% Conversion	.57	1.7	3.56	7.56	.73	1.3	3.2	12.6
Rate, %/Hrs.	1.14	1.13	.89	1.26	2.9	2.6	3.2	2.8
PROPERTIES								
Molecular Wt.	648	716	823	912	553	815	706	891
Wt.% Oxygen	9.02	7.46	5.70	4.49	10.42	6.37	6.75	5.91
O_2 Equivalent Weight	354	429	562	713	307	503	474	542
O_2/Molecule	1.83	1.66	1.48	1.28	1.8	1.62	1.49	1.65

the reaction environment during the batch runs were taking place, and that these changes were apparently having an adverse effect on the termination reaction. These ester products were homogeneous, clear, lightly colored oils, whose infra-red spectra were similar to previous DMAB initiated copolymers.

Saponification with the standard alkaline hydrolysis procedure showed the presence of the anticipated potassium salt of the carboxyl terminated copolymer and also a different substance. The copolymer salt was soluble in n-butanol while the other substance was water soluble and methanol insoluble.

The n-butanol soluble copolymer fraction was converted from salt to acid form, dried and submitted for molecular weight and neutralization equivalent determination. The water soluble fraction was analyzed by titration with aqueous acid. The results of these determinations are tabulated in Table III.

From the data it appears that the cause of high ester functionality in the early stages of the polymerization is the presence of those ester bearing groups which are water soluble upon saponifaction. The n-butanol soluble copolymer is not markedly higher in functionality during the early stages of the polymerization, although a downward trend in COOH functionality with time is seen in the 90°C runs.

The exact origin of this "water soluble" fraction is not completely understood. As the batch polymerization proceeds additional small amounts of this material are made, so it is surmised that it is derived from small amounts of methyl methacrylate generated by initiator radical-radical disproportionation. It should be noted that in a high conversion continuous process the amount of such material generated would be quite small.

The more significant point is that for every methyl methacrylate molecule produced by disproportionation, a methyl isobutyrate molecule also forms. The latter molecule is a chain transfer agent. We are endeavoring to better establish the validity of this explanation. If the new iniator DTAB, also results in a polymer of functionality unity, we will conclude that the transfer agent is an alkyl isobutyrate.

C. Synthesis of DTAB.

As stated previously, it is desirable to utilize an initiator for this copolymerization of such a structure that chain transfer involving abstraction of a hydrogen atom

TABLE III

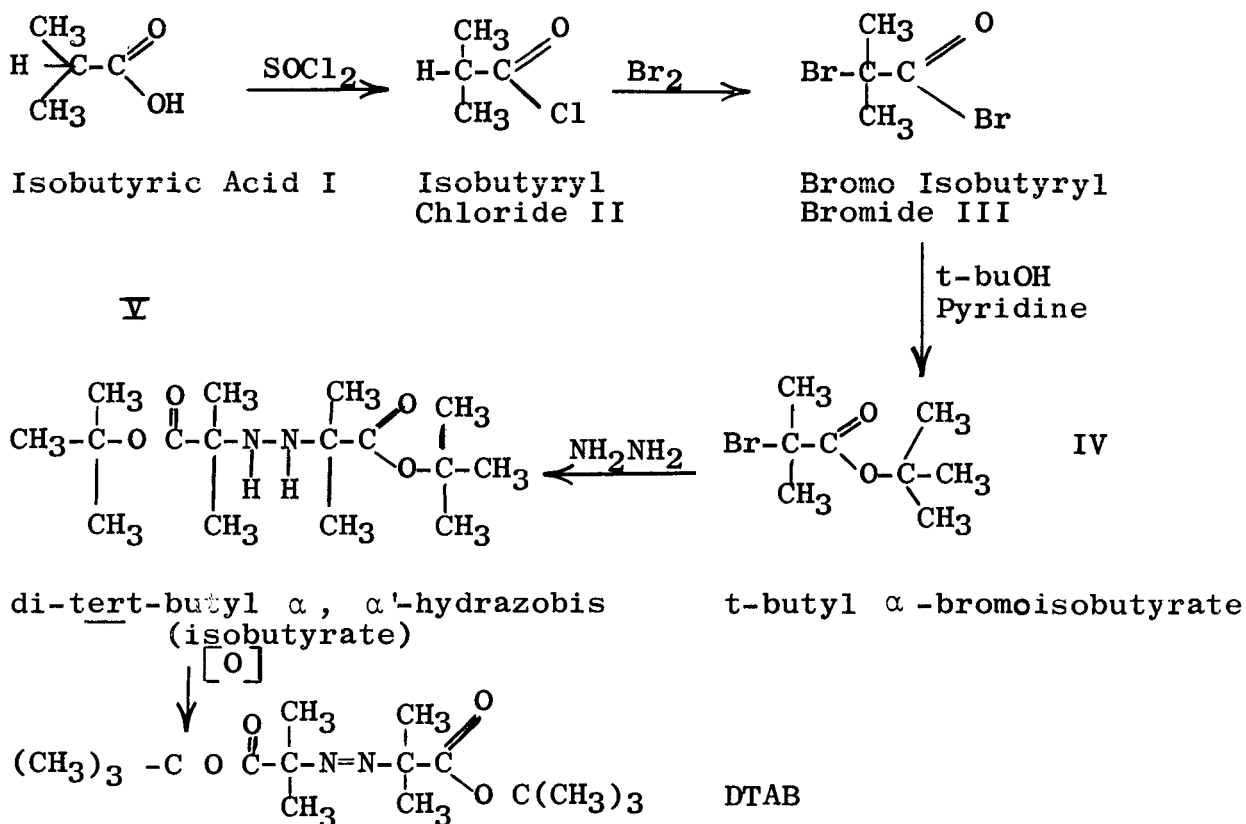### EFFECT OF REACTION TIME ON COOH FUNCTIONALITY

Sample	23 EMS 33	34	31	32	44	41	42	37
Wt. Sample, gms.	1.34	5.98	14.93	33.98	2.39	4.83	7.50	20.83
Wt. Butanol Sol. Fraction	1.06	2.72*	12.71	16.09*	1.95	4.16	6.82	18.52
Wt. Water Sol. Fraction	**	**	**	**	0.4	1.05	1.40	2.30
Neutralization Equiv. Butanol Sol. Fraction	858	792	751	863	556	676	578	745
Water Sol. Fraction***	-	-	-	-	243	221	197	240
Mol. Wt. Butanol Sol. Fraction In CHCl3	1093	1067	1053	1150	-	999	851	929
In THF	907	843	830	943	640	759	617	719
Functionality (COOH) On CHCl3 M. Wt.	1.28	1.35	1.40	1.33	-	1.48	1.48	1.25
On THF M. Wt.	1.06	1.07	1.10	1.09	1.15	1.12	1.07	0.96

*   Some Material lost on work-up
**   Not quantitatively isolated
*** No Mol. Wt. Det'n Available

from the structure or its decomposition products is at an
absolute minimum. DTAB, ditertiary butyl, α, α' azobis
(isobutyrate) may be such a compound. The following
reaction scheme is being examined as a possible route to
this compound.

Isobutyric Acid I   Isobutyryl   Bromo Isobutyryl
                Chloride II   Bromide III

t-buOH
Pyridine

di-tert-butyl α, α'-hydrazobis   t-butyl α-bromoisobutyrate
        (isobutyrate)

DTAB

All steps in this synthesis have been completed
without difficulty up to the coupling reaction which is being
examined at present. The oxidation of the coupled product V
should be quite facile, judging from the ease with which this
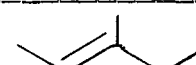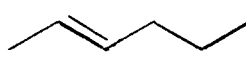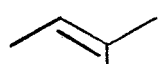reaction was carried out in the synthesis of DMAB.
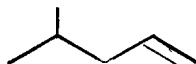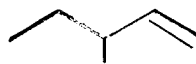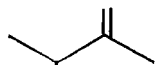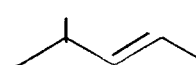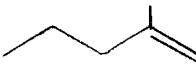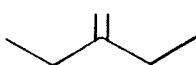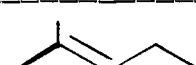
VI. PLANS FOR FUTURE WORK

Ethylene-neohexene copolymerizations will be carried
out using the continuous, tube reactor, to determine the
effect of steady state operation on product quality. DMAB
initiator will be used initially.

Curing studies will be performed on prepolymer samples made with DMAB in batch equipment.

The proposed reaction scheme for the synthesis of DTAB initiator will be investigated more thoroughly. If successful, copolymerization runs will be made as soon as possible with this initiator.

Previous efforts to use compounds such as dithio-dibutyric acid in conjunction with various azo initiators to control functionality were complicated by the limited solubility of the sulfur compound. The tertiary butyl ester of dithio-dibutyric acid will be made and used in copolymerizations.

TABLE 1 A
BOILING POINTS AND STRUCTURAL FORMULAE OF HEXENE ISOMERS

Name	°C Boiling Point	Structural Formula
3,3-Dimethylbutene-1 (Neohexene)	41.2	
4-Methylpentene-1	53.6	
3-Methylpentene-1	53.6	(Sample A)
2,3-Dimethylbutene-1	56.0	
4-Methylpentene-2	57.7	(Sample B)
2-Methylpentene-1	61.5	
Hexene-1	63.5	
2-Ethylbutene-1	66.2	
2-Methylpentene-2	67.2	(Sample D)
Hexene-3	67.5	
3-Methylpentene-2	67.6	
Hexene-2	67.9	
2,3-Dimethylbutene-2	73.0	(Sample E)

GAS CHROMATOGRAPHIC ANALYSIS
OF NEOHEXENE MONOMER

Figure 1

arrows at retention times
of other hexene isomers

sample injected
10,000x attenuation

change to
20x attenuation

Retention Time, min. ➡

sample injected
5000x attenuation

Retention Time, min. ➡